



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/386	A1	(11) International Publication Number: WO 98/06808 (43) International Publication Date: 19 February 1998 (19.02.98)
(21) International Application Number: PCT/US96/12962 (22) International Filing Date: 9 August 1996 (09.08.96) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HERBOTS, Ivan, Maurice, Alfons, Jan [BE/BE]; Hellegat 11, B-9230 Wetteren (BE). BAECK, Andre, Cesar [BE/BE]; Putsesteenweg 273, B-2820 Bonheiden (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: DETERGENT COMPOSITIONS COMPRISING ALKALINE PECTIN DEGRADING ENZYME (57) Abstract The present invention relates to detergent compositions, including dishwashing, hard surface cleaning and laundry compositions containing an alkaline pectin degrading enzyme for improved overall cleaning performance and enhanced stain/soil removal benefits and in particular improved removal of plant, dried-on fruit and vegetable juice soils/stains.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**DETERGENT COMPOSITIONS COMPRISING ALKALINE
PECTIN DEGRADING ENZYME**

Field of the Invention

The present invention relates to detergent compositions, including dishwashing, hard surface cleaning and laundry compositions comprising an alkaline pectin degrading enzyme.

Background of the invention

The overall performance of a detergent product for use in washing or cleaning method such as laundry, dishwashing or hard surface cleaning, is judged by a number of factors, including the ability to remove soils and the ability to prevent redeposition of the soils, or the breakdown products of the soils on the articles in the wash.

Removal of stains stemming from plants, wood, mould-clay based soil and fruits is one of today's toughest cleaning task; in particular with the trends to move to low wash temperatures. These stains typically contain complex mixtures of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components.

Plant based soils are additionally accompanied with amylose, sugars and their derivatives.

Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils. The substrates can be fabrics, dishware or hard surfaces.

Pectic substances are found in, for example, fruit juices. The pectic substances act to hold dispersed particulates in suspension in such fruit juices, which will tend to be viscous and opaque in nature. Pectic enzymes are commonly used in the fruit/vegetable juice processing industry in the clarification of juices by breakdown of the pectic substances therein (depectinisation).

The use of pectin enzyme is also recognised for the cleaning of contact lenses (US 4,710,313 - J60196724).

Enzymes having a pectinase activity are described in DE 36 35 427 to increase the capacity of the detergent for removing inorganic dirt, e.g. sludges, from laundry without damaging the fibres and without discoloration to allow the use of zeolites and polycarbonate builders which have a lower capacity for dispersing inorganic materials than the phosphates. Benefits for the use of pectin enzymes in detergent formulations, particularly those designed for use in laundry, dishwashing and household cleaning operations have been recognised in WO95/25790. JP 60226599 describes detergent composition comprising conventional detergent actives and a cellulase and hydrolase such as hemicellulase, pectinase, amylase or protease. The combination of cellulase and hydrolase is said to give a

good washing effect on inorganic fouling together with enzymatic activity.

WO95/09909 describes an enzyme preparation comprising modified enzyme selected from the group of amylase, lipase, oxidoreductase, pectinase or hemicellulase; the modified enzyme having an improved performance due to an alkaline pI and/or increased surface activity obtained by chemical modification or amino acid substitution. Modified pectin and/or pectolytic and/or hemi-cellulolytic and /or lipolytic enzymes are applied advantageously in the papermaking industry and modified amylase and/or lipase in laundry and dishwashing.

It is an object of the present invention to provide laundry, dishwashing or household detergent compositions which provide improved soil / stain removal benefits when used in washing and cleaning operations.

According to the present invention, it has now been surprisingly found that the pectin degrading enzymes with an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its optimum activity, at a pH ranging from 7 to 11 and in particular pectin degrading enzyme having an optimum activity at a pH ranging from 7 to 11; improve significantly the removal of a broad range of plant and fruit based stains and enhance the realistic item cleaning profile of the detergent compositions.

Indeed, the inclusion of alkaline pectin degrading enzyme provides in particular improved removal of dried-on fruit and vegetables juice soils/stains.

In addition, it has been found that the alkaline pectin degrading enzyme presents improved compatibility and enhanced activity in the wash solution thereby providing improved removal of body, dried-on fruit and vegetables

juice soils/stains, especially when stemming from heavy duty laundry or dishwashing compositions. It has also been found that the alkaline pectin degrading enzyme demonstrates a better compatibility with detergent matrix, e.g. during product process and shelf life.

Furthermore, it has also been surprisingly been found that the inclusion of dispersants, particularly organic polymer dispersants, is of great value in detergent compositions containing alkaline pectin degrading enzymes. The dispersants aid dispersion of the breakdown products of the enzymatic soil degradation, thus preventing their redeposition on articles on the wash.

Improved cleaning performance has been also observed when the alkaline pectin degrading enzymes are combined with other detergent enzyme. Enzymatic bleaching system or conventional activated bleach system together with alkaline pectin degrading enzymes provides enhanced performance benefits on a wider range of stains.

Furthermore, polymers providing dye transfer inhibition combined with alkaline pectin degrading enzymes results in improved whiteness maintenance and /or soil release properties.

Summary of the invention

The present invention relates to detergent compositions, including dishwashing, hard surface cleaning and laundry compositions comprising an alkaline pectin degrading enzyme for improved overall cleaning performance and enhanced stain / soil removal benefits and in particular improved removal of plant, dried-on fruit and vegetables juice soils/stains.

In a preferred embodiment of the present invention, the detergent composition further comprises a dispersant, a bleaching system, another detergent enzyme and/or a dye transfer polymer.

Detailed description of the invention

The alkaline pectin degrading enzyme

An essential component of the detergent compositions of the invention is an alkaline pectin degrading enzyme. By pectin degrading enzyme it is meant herein any enzyme which acts to break down pectic substances and pectin related substances. Pectic substances may be found in plant tissues, and are common constituents of fruit juices such as orange, tomato and grape juices. Pectic substances contain galacturonic acids and/or their derivatives.

The term "alkaline" is intended to cover a pectin degrading enzyme having an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its optimum activity, at a pH ranging from 7 to 11 and preferably to cover pectin degrading enzyme having an optimum activity at a pH ranging from 7 to 11. The enzymatic activity can be measured according to the "Measurement of viscosity" as described by K. Horikoshi in Agr. Biol. Chem, Vol 36(2), 286.

The term "pectin degrading enzyme" is intended to encompass polygalacturonase (EC 3.2.1.15) exo-polygalacturonase (EC 3.2.1.67), exo-poly-alpha-galacturonidase (EC 3.2.1.82), pectin lyase (EC 4.2.2.10), pectin esterase (EC 3.2.1.11), pectate lyase (EC 4.2.2.2), exo-polygalacturonate lyase (EC 4.2.2.9) and hemicellulases such as endo-1,3- β -xylosidase (EC 3.2.1.32), xylan-1,4- β -xylosidase (EC 3.2.1.37) and α -L-arabinofuranosidase (EC

3.2.1.55). The alkaline pectin degrading enzymes are natural mixtures of the above mentioned enzymatic activities.

Pectin enzymes therefore include the pectin methylesterases which hydrolyse the pectin methyl ester linkages, polygalacturonases which cleave the glycosidic bonds between galacturonic acid molecules, and the pectin transeliminases or lyases which act on the pectic acids to bring about non-hydrolytic cleavage of α -1 \rightarrow 4 glycosidic linkages to form unsaturated derivatives of galacturonic acid.

Pectic substances include pectins and pectic acids. pectins are, in general, polymers made up of chains of galacturonic acids joined by α -1 \rightarrow 4 glycosidic linkages. Typically, in natural pectins approximately two-third of the carboxylic acid groups are esterified with methanol. Partial hydrolysis of these methyl esters gives low methoxyl pectins, which tend to form gels with calcium ions. Complete ester hydrolysis gives pectic acids.

Pectin degrading enzyme is incorporated into the compositions in accordance with the invention preferably at a level of from 0.0001 % to 2 %, more preferably from 0.0005% to 0.5%, most preferred from 0.001 % to 0.1 % pure enzyme by weight of the total composition.

Pectin degrading enzyme can be produced by the so called wild-type organism or by any host organism in which the gene responsible for the production of the pectin enzyme, has been cloned and expressed.

Alkaline pectin enzymes are produced by alkalophilic microorganisms e.g. bacterial, fungal and yeast microorganisms such as *Bacillus* species. Preferred microorganisms are *Bacillus firmus*, *Bacillus circulans* and

Bacillus subtilis as described in JP 56131376 and JP 56068393. Alkaline pectin decomposing enzymes include galacturan-1,4- α -galacturonase (EC 3.2.1.67), polygalacturonase activities (EC3.2.1.15, pectin esterase (EC 3.1.1.11), pectate lyase (EC 4.2.2.2) and their iso enzymes and they can be produced by the *Erwinia* species. Preferred are *E. chrysanthemi*, *E. carotovora*, *E. amylovora*, *E. herbicola*, *E. dissolvens* as described in JP 59066588, JP 63042988 and in World J. Microbiol. Microbiotechnol. (8, 2, 115-120) 1992. Said alkaline pectin enzymes can also be produced by *Bacillus* species as disclosed in JP 73006557 and Agr. Biol. Chem. (1972), 36(2) 285-93.

Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

Dispersants

It has also been surprisingly been found that the inclusion of dispersants, particularly organic polymer dispersants, is of great value in detergent compositions containing alkaline pectin degrading enzymes. The dispersants aid dispersion of the breakdown products of the enzymatic soil degradation, thus preventing their redeposition on articles on the wash.

Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the cleaning compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for

example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO_3 (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C_{16} - C_{18} dimethyl amine oxide, C_{12} - C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12} - C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14} - C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Detergent enzymes

Especially improved removal of a broad range of plant and fruit based stains is achieved with a combination of alkaline pectin degrading enzymes with other detergent enzymes.

Synergistic effects are observed with detergent compositions comprising an alkaline pectin degrading enzyme and a cellulase, xylanase and/or protease.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Suitable xylanases include the commercail available xylanases like Pulpzyme HB and SP431 (Novo Nordisk), Lyxasan (Gist-Brocades), Optipulp and Xylanase (Solvay).

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE[®], DURAZYM[®] and SAVINASE[®] from Novo and MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] (protein engineered Maxacal) from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. Other preferred proteases include those of WO 95/10591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens*

subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO91/06637 and the protease BLAP[®] described in WO91/02792.

Improved plant and fruit stains / soils removal is observed with detergent compositions of the present invention further comprising starch-, sugar- and their derivatives-degrading enzymes such as amylase, gluco amylase, dextranase, pullulanase, invertase, laccase insulinase.

Suitable amylases (α and/or β) to be included in the detergent compositions of the present invention are : WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994, WO95/10603, Novo Nordisk A/S, published April 20, 1995 and WO96/05295, genencor, published February 22, 1996. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox Am[®] described in WO 94/18314, published August 18, 1994 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Examples of commercial α -amylases products are Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at

least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

Other carbohydrases combined with alkaline pectin degrading enzymes show synergistic performance benefits, such as β -glucanase (lichenase, laminarase) and exo-glucanase (lignase, tannase, pentosanase, malanase and hemi-cellulase)

Finally, combinations of enzymes hydrolysing fat and waxes such as lipases, cutinases and wax esterases and alkaline pectin degrading enzymes provide synergistic improved plant and fruit stains / soils removal

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism Pseudomonas fluorescent IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo) which have found to be very effective when

used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for

use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Bleaching agent

It has been found that a wider range of plant and/or fruit based stains / soils removal is achieved with detergent compositions comprising an enzymatic bleaching system or conventional activated bleach system in addition to the alkaline pectin degrading enzyme.

Bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

The bleaching agent component for use herein can be any of the bleaching agents useful for cleaning compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-

oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxypropionic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "stain and solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Another oxidase to be included in the detergent composition of the present invention is laccase.

Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Dye transfer inhibition

Further enhanced whiteness maintenance and/or soil release properties have been observed when the detergent compositions of the present invention include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

Polymeric dye transfer inhibiting agents

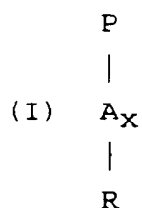
The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

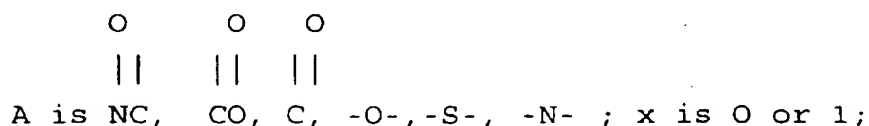
Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

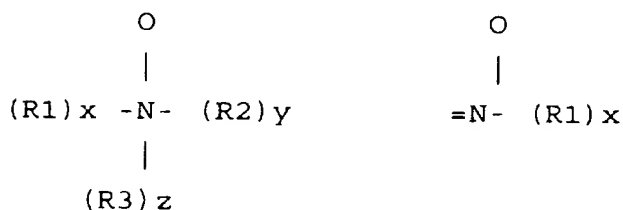


wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-

oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $\text{PKa} < 10$, preferably $\text{PKa} < 7$, more preferred $\text{PKa} < 6$. The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1,000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while

not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average

about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-pending patent application 94870213.9

Detergent components

The cleaning compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of

the composition, and the nature of the cleaning operation for which it is to be used.

The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form.

The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning operations.

Such compositions containing pectin degrading enzyme can provide fabric cleaning, stain removal, whiteness maintenance, softening, color appearance and dye transfer inhibition when formulated as laundry detergent compositions.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds

suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides.

A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Surfactant system

The cleaning compositions according to the present invention comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of cleaning compositions in accord with the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from

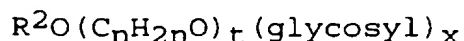
about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear

alcohol with 3.0 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro™ EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA 030 or 050 (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures

thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

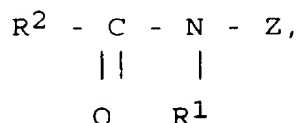
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products

consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

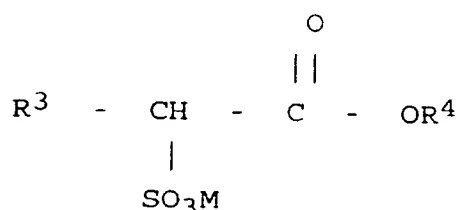


wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing

sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal

cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the cleaning compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k-CH_2COO-M^+$ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-

forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

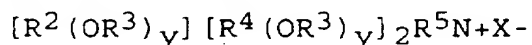
Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference). When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18}

alkyl polyethoxylate (2.25) sulfate ($C_{12}-C_{18}E(2.25)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (3.0) sulfate ($C_{12}-C_{18}E(3.0)M$), and $C_{12}-C_{18}$ alkyl polyethoxylate (4.0) sulfate ($C_{12}-C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

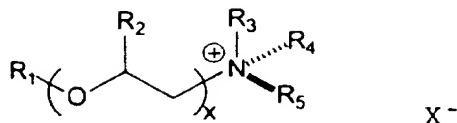
The cleaning compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



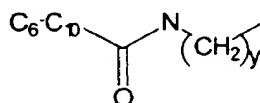
wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :



Formula II

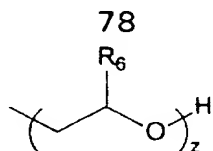
y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxyated alkyl of the formula III,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

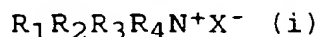
R6 is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

R₁ is C₈, C₁₀ or mixtures thereof, x=0,

R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R_1 is C_8-C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl. The preferred alkyl chain length for R_1 is $C_{12}-C_{15}$ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2 , R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
 coconut methyl dihydroxyethyl ammonium chloride or bromide;
 decyl triethyl ammonium chloride;
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 lauryl dimethyl benzyl ammonium chloride or bromide;
 lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
 choline esters (compounds of formula (i) wherein R_1 is $CH_2-CH_2-O-C-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

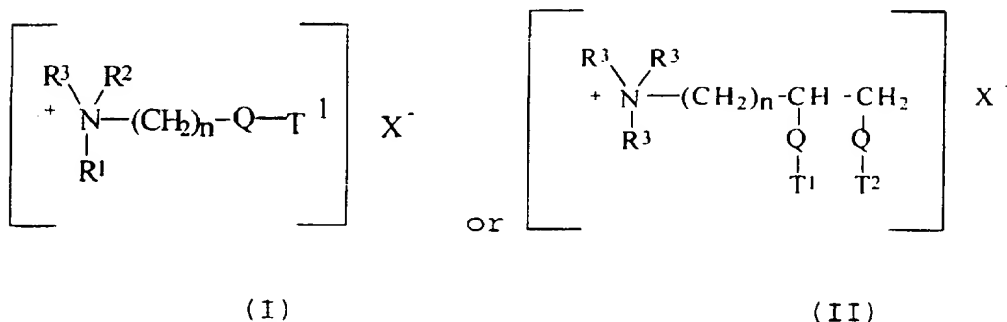
Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
- 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallowoyloxyethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

R¹ is (CH₂)_n-Q-T² or T³;

R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;

R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;

R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;

n and m are integers from 1 to 4; and

X⁻ is a softener-compatible anion.

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammonio propane chloride; and mixtures of any of the above materials.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

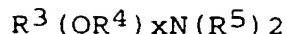
When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

0

↑



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

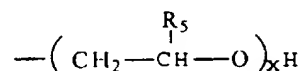
The cleaning composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain or $R_4X(CH_2)_n$, X is -O-, -C(O)NH- or -NH-, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C_8 - C_{10}

oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

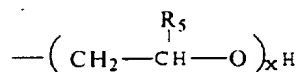
Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R_1 and R_2 are C_1 - C_8 alkylchains or



R_3 is either a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain, or R_3 is $R_4X(CH_2)_n$, whereby X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_4 - C_{12} , n is between 1 to 5, preferably 2-3. R_5 is H or C_1 - C_2 alkyl and x is between 1 to 6.

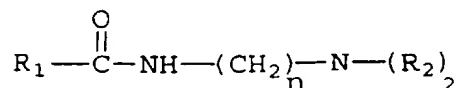
R_3 and R_4 may be linear or branched; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $R_1R_2R_3N$ where R_1 is a C_6 - C_{12} alkyl chain, R_2 and R_3 are C_1 - C_3 alkyl or



where R_5 is H or CH_3 and $x = 1-2$.

Also preferred are the amidoamines of the formula:



wherein R_1 is C_6 - C_{12} alkyl; n is 2-4, preferably n is 3; R_2 and R_3 is C_1 - C_4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C_8 -10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles

propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Color care benefits

Technologies which provide a type of color care benefit can also be included. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2.

Builder system

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates,

cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_4EDDS . Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a

liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in cleaning compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of

polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

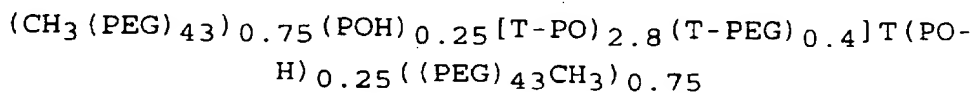
Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' - bis-(2,4-dianilino-s-tri-azin-6 ylamino)stilbene-2-

sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' -disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the pectin enzyme. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described

in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Softening agents

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide

materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being

treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

- LAS : Sodium linear C₁₂ alkyl benzene sulphonate
- TAS : Sodium tallow alkyl sulphate
- CXYAS : Sodium C_{1X} - C_{1Y} alkyl sulfate
- 25EY : A C₁₂-C₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
- CX YEZ : A C_{1X} - C_{1Y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
- XYE ZS : C_{1X} - C_{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole

- QAS : $R_2 \cdot N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}-C_{14}$
- Soap : Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut oils.
- Nonionic : $C_{13}-C_{15}$ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF GmbH.
- CFAA : $C_{12}-C_{14}$ alkyl N-methyl glucamide
- TFAA : $C_{16}-C_{18}$ alkyl N-methyl glucamide.
- TPKFA : $C_{12}-C_{14}$ topped whole cut fatty acids.
- DEQA : Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.
- SDASA : 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.
- Neodol 45-13 : $C_{14}-C_{15}$ linear primary alcohol ethoxylate, sold by Shell Chemical CO.
- Silicate : Amorphous Sodium Silicate ($SiO_2:Na_2O$ ratio = 2.0)
- NaSKS-6 : Crystalline layered silicate of formula $\delta-Na_2Si_2O_5$.
- Carbonate : Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm .

- Bicarbonate : Anhydrous sodium bicarbonate with a particle size between 400 μm and 1200 μm .
- STPP : Anhydrous sodium tripolyphosphate
- MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
- PA30 : Polyacrylic acid of average molecular weight of approximately 8,000.
- Terpolymer : Terpolymer of average molecular weight approx. 7,000, comprising acrylic:maleic:ethylacrylic acid monomer units at a weight ratio of 60:20:20
- 480N : Random copolymer of 3:7 acrylic/methacrylic acid, average molecular weight about 3,500.
- Polyacrylate : Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
- Zeolite A : Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers
- Citrate : Tri-sodium citrate dihydrate of activity 86,4% with a particle size distribution between 425 μm and 850 μm .
- Citric : Anhydrous citric acid

PB1 : Anhydrous sodium perborate monohydrate
bleach, empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$

PB4 : Anhydrous sodium perborate tetrahydrate

Percarbonate : Anhydrous sodium percarbonate bleach of
empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$

TAED : Tetraacetyl ethylene diamine.

NOBS : Nonanoyloxybenzene sulfonate in the form
of the sodium salt.

Photoactivated : Sulfonated zinc phtlocyanine
Bleach encapsulated in dextrin soluble polymer.

PAAC : Pentaamine acetate cobalt(III) salt.

Paraffin : Paraffin oil sold under the tradename
Winog 70 by Wintershall.

BzP : Benzoyl Peroxide.

Pectin : Pectin degrading enzyme produced by
degrading Bacillus P-4-N as described in Agr.
enzyme Biol. Chem. (1972) 36(2), 285-93.

Protease : Proteolytic enzyme sold under the
tradename Savinase, Alcalase, Durazym by
Novo Nordisk A/S, Maxacal, Maxapem sold
by Gist-Brocades and proteases described
in patents WO91/06637 and/or WO95/10591
and/or EP 251 446.

- Amylase : Amylolytic enzyme sold under the tradename Purafact Ox Am^R described in WO 94/18314, sold by Genencor; Termamyl[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S and those described in WO95/26397.
- Lipase : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S
- Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
- CMC : Sodium carboxymethyl cellulose.
- HEDP : 1,1-hydroxyethane diphosphonic acid.
- DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060.
- PVNO : Poly(4-vinylpyridine)-N-Oxide.
- PVPVI : Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone.
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.

Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

Granular Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form

SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone.

SRP 2 : Diethoxylated poly (1,2 propylene terephthalate) short block polymer.

Sulphate : Anhydrous sodium sulphate.

HMWPEO : High molecular weight polyethylene oxide

PEG : Polyethylene glycol.

BTA : Benzotriazole

Bismuth nitrate : Bismuth nitrate salt

NaDCC : Sodium dichloroisocyanurate

Encapsulated perfume particles : Insoluble fragrance delivery technology utilising zeolite 13x, perfume and a dextrose/glycerin agglomerating binder.

KOH : 100% active solution of Potassium Hydroxide.

pH : Measured as a 1% solution in distilled water at 20°C.

Example 1

The following laundry detergent compositions were prepared in accord with the invention:

	I	II	III	IV	V	VI
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
QAS	-	0.8	0.8	-	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Pectin	0.005	0.01	0.05	0.01	0.02	0.08
degrading enzyme						
Protease	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026
Amylase	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15	15	15	15	15	15
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone	0.5	0.5	0.5	0.5	0.5	0.5
antifoam						
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions of bulk density 750 g/litre were prepared in accord with the invention:

	I	II	III
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3
PB4	5.0	12.7	-
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Pectin degrading enzyme	0.001	0.02	0.0006
Protease	0.0026	0.008	0.045
Lipase	0.003	0.003	0.003
Cellulase	0.0006	0.0006	0.0006
Amylase	0.0009	0.0009	0.0009
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm

WO 98/06808

62

PCT/US96/12962

Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Encapsulated perfume particles	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%			

Example 3

The following detergent formulations, according to the present invention were prepared, where I is a phosphorus-containing detergent composition, II is a zeolite-containing detergent composition and III is a compact detergent composition:

	I	II	III
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Pectin degrading enzyme	0.05	0.05	0.01
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009

WO 98/06808

64

PCT/US96/12962

Amylase	0.002	0.003	0.001
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Pectin degrading enzyme	0.05	0.005	0.02
Protease	0.026	0.016	0.047
Lipase	0.009	0.009	0.009

WO 98/06808

66

PCT/US96/12962

Amylase	0.005	0.005	0.005
Cellulase	0.006	0.006	0.006
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 5

The following detergent formulations, according to the present invention were prepared:

	I	II	III	IV
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DETPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Pectin degrading enzyme	0.08	0.04	0.05	0.01
Protease	0.008	0.01	0.026	0.026
Amylase	0.007	0.004	-	0.002
Lipase	0.004	0.002	0.004	0.002
Cellulase	0.0015	0.0005	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Balance	100	100	100	100
(Moisture and Miscellaneous)				

Example 6

The following detergent formulations, according to the present invention were prepared:

	I	II	III	IV
Blown Powder				
Zeolite A	30.0	22.0	6.0	6.7
Na SkS-6	-	-	-	3.3
Polycarboxylate	-	-	-	7.1
Sodium sulfate	19.0	5.0	7.0	-
MA/AA	3.0	3.0	6.0	-
LAS	14.0	12.0	22.0	21.5
C45AS	8.0	7.0	7.0	5.5
Cationic	-	-	-	1.0
Silicate	-	1.0	5.0	11.4
Soap	-	-	2.0	-
Brightener 1	0.2	0.2	0.2	-
Carbonate	8.0	16.0	20.0	10.0
DETPMP	-	0.4	0.4	-
Spray On				
C45E7	1.0	1.0	1.0	3.2
Dry additives				
PVPVI/PVNO	0.5	0.5	0.5	-
Pectin degrading enzyme	0.005	0.01	0.01	0.005
Protease	0.052	0.01	0.01	0.01
Lipase	0.009	0.009	0.009	0.009
Amylase	0.001	0.001	0.001	0.001
Cellulase	0.0002	0.0002	0.0002	0.0002
NOBS	-	6.1	4.5	3.2
PB1	1.0	5.0	6.0	3.9
Sodium sulfate	-	6.0	-	to balance
Balance (Moisture and Miscellaneous)	100	100	100	

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Pectin degrading enzyme	0.005	0.01	0.08
Protease	0.01	0.01	0.01

WO 98/06808

70

PCT/US96/12962

Lipase	0.009	0.009	0.009
Amylase	0.005	0.005	0.005
Cellulase	0.002	0.002	0.002
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following high density detergent formulations, according to the present invention were prepared:

	I	II
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Pectin degrading enzyme	0.02	0.05
Protease	0.04	0.04
Lipase	0.009	0.009
Cellulase	0.004	0.004
Amylase	0.005	0.005
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

Example 9

The following granular detergent formulations, according to the present invention were prepared:

	I	II	III	IV	V
LAS	21.0	25.0	18.0	18.0	-
Coco C12-14 AS	-	-	-	-	21.9
AE3S	-	-	1.5	1.5	2.3
Decyl dimethyl hydroxyethyl NH4+Cl	-	0.4	0.7	0.7	0.8
Nonionic	1.2	-	0.9	0.5	-
Coco C12-14 Fatty Alcohol	-	-	-	-	1.0
STPP	44.0	25.0	22.5	22.5	22.5
Zeolite A	7.0	10.0	-	-	8.0
MA/AA	-	-	0.9	0.9	-
SRP1	0.3	0.15	0.2	0.1	0.2
CMC	0.3	2.0	0.75	0.4	1.0
Carbonate	17.5	29.3	5.0	13.0	15.0
Silicate	2.0	-	7.6	7.9	-
Pectin degrading enzyme	0.005	0.01	0.007	0.01	0.01
Protease	0.007	0.007	0.007	0.007	0.007
Amylase	-	0.004	0.004	0.004	0.004
Lipase	0.003	0.003	0.003	-	-
Cellulase	-	0.001	0.001	0.001	0.001
NOBS	-	-	-	1.2	1.0
PB1	-	-	-	2.4	1.2
Diethylene triamine penta acetic acid	-	-	-	0.7	1.0
Diethylene triamine penta methyl phosphonic acid	-	-	0.6	-	-
Mg Sulfate	-	-	0.8	-	-
Photoactivated bleach	45	50	15	45	42
	ppm	ppm	ppm	ppm	ppm

Brightener 1	0.05	-	0.04	0.04	0.04
Brightener 2	0.1	0.3	0.05	0.13	0.13
Water and Minors	up to 100%				

Example 10

The following liquid detergent formulations, according to the present invention were prepared:

	I	II	III	IV	V	VI	VII	VIII
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
QAS	-	-	-	-	3.0	1.0	-	-
TPKFA	2.0	-	13.0	2.0	-	15.0	7.0	7.0
Rapeseed fatty acids	-	-	-	5.0	-	-	4.0	4.0
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/ tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Mono Ethanol Amine	-	-	-	5.0	-	-	9.0	9.0
Tri Ethanol Amine	-	-	8	-	-	-	-	-
NaOH (pH)	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2
Ethoxylated tetraethylene pentamine	0.5	-	0.5	0.2	-	-	0.4	0.3
DETPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
SRP 2	0.3	-	0.3	0.1	-	-	0.2	0.1
PVNO	-	-	-	-	-	-	-	0.10
Pectin degrading enzyme	.005	.005	.005	.005	.05	0.07	0.02	0.01
Protease	.005	.005	.004	.003	.008	.005	.003	.006

Lipase	-	.002	-	.001	-	-	.003	.003
Amylase	.002	.002	.005	.004	.002	.008	.005	.005
Cellulase	-	-	-	.00	-	-	.00	.00
				1			2	1
Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	-
Ca chloride	-	0.01	-	0.01	-	-	-	-
		5						
Bentonite	-	-	-	-	4.0	4.0	-	-
clay								
Suspending	-	-	-	-	0.6	0.3	-	-
clay SD3								
Balance	100	100	100	100	100	100	100	100
Moisture and								
Miscellaneous								

Example 11

Granular fabric cleaning compositions which provide "softening through the wash" capability were prepared in accord with the present invention :

	I	II
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Pectin degrading enzyme	0.01	0.01
Protease	0.02	0.1
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
Water/minors	Up to 100%	

Example 12

The following rinse added fabric softener composition was prepared in accord with the present invention :

Softener active	20.0
Pectin degrading enzyme	0.01
Amylase	0.001
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
CaCl ₂	0.20
Perfume	0.90
Water / minors	Up to 100%

Example 13

The following fabric softener composition was prepared in accord with the present invention :

	I	II	III
DEQA	2.6	19.0	-
SDASA	-	-	70.0
Stearic acid of IV=0	0.3	-	-
Neodol 45-13	-	-	13.0
Hydrochloride acid	0.02	0.02	-
Ethanol	-	-	1.0
PEG	-	0.6	-
Pectin degrading enzyme	0.005	0.05	0.01
Perfume	1.0	1.0	0.75
Digeranyl Succinate	-	-	0.38
Silicone antifoam	0.01	0.01	-
Electrolyte	-	600ppm	-
Dye	100ppm	50ppm	0.01
Water and minors	100%	100%	

Example 14

Syndet bar fabric cleaning compositions were prepared in accord with the present invention :

	I	II	III	IV
C26 AS	20.00	20.00	20.00	20.00
CFAA	5.0	5.0	5.0	5.0
LAS (C11-13)	10.0	10.0	10.0	10.0
Sodium carbonate	25.0	25.0	25.0	25.0
Sodium pyrophosphate	7.0	7.0	7.0	7.0
STPP	7.0	7.0	7.0	7.0
Zeolite A	5.0	5.0	5.0	5.0
CMC	0.2	0.2	0.2	0.2
Polyacrylate (MW 1400)	0.2	0.2	0.2	0.2
Coconut monethanolamide	5.0	5.0	5.0	5.0
Pectin degrading enzyme	0.1	0.1	0.15	0.2
Amylase	0.01	0.02	0.01	0.01
Protease	0.3	-	0.5	0.05
Brightener, perfume	0.2	0.2	0.2	0.2
CaSO4	1.0	1.0	1.0	1.0
MgSO4	1.0	1.0	1.0	1.0
Water	4.0	4.0	4.0	4.0

Filler* : balance to 100%

*Can be selected from convenient materials such as CaCO₃, talc, clay (Kaolinite, Smectite), silicates, and the like.

Example 15

The following compact high density (0.96Kg/l) dishwashing detergent compositions I to VI were prepared in accord with the present invention:

	I	II	III	IV	V	VI
STPP	-	-	49.0	38.0	-	-
Citrate	33.0	17.5	-	-	54.0	25.4
Carbonate	-	17.5	-	20.0	14.0	25.4
Silicate	33.0	14.8	20.4	14.8	14.8	-
Metasilicate	-	2.5	2.5	-	-	-
PB1	1.9	9.7	7.8	14.3	7.8	-
PB4	8.6	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7
Nonionic	1.5	2.0	1.5	1.5	1.5	2.6
TAED	4.8	2.4	2.4	-	2.4	4.0
HEDP	0.8	1.0	0.5	-	-	-
DETPMP	0.6	0.6	-	-	-	-
PAAC	-	-	-	0.2	-	-
BzP	-	-	-	4.4	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.2
Pectin degrading enzyme	0.07	0.05	0.1	0.1	0.08	0.01
Protease	0.075	0.05	0.10	0.10	0.08	0.01
Lipase	-	0.001	-	0.005	-	-
Amylase	0.01	0.005	0.015	0.015	0.01	0.0025
BTA	0.3	0.3	0.3	0.3	0.3	-
Bismuth Nitrate	-	0.3	-	-	-	-
PA30	4.0	-	-	-	-	-
Terpolymer	-	-	-	4.0	-	-
480N	-	6.0	2.8	-	-	-
Sulphate	7.1	20.8	8.4	-	0.5	1.0
pH (1% solution)	10.8	11.0	10.9	10.8	10.9	9.6

Example 16

The following granular dishwashing detergent compositions examples I to IV of bulk density 1.02Kg/L were prepared in accord with the present invention :

	I	II	III	IV	V	VI
STPP	30.0	30.0	30.0	27.9	34.5	26.7
Carbonate	30.5	30.5	30.5	23.0	30.5	2.80
Silicate	7.4	7.4	7.4	12.0	8.0	20.3
PB1	4.4	4.4	4.4	-	4.4	-
NaDCC	-	-	-	2.0	-	1.5
Nonionic	0.75	0.75	0.75	1.9	1.2	0.5
TAED	1.0	1.0	-	-	1.0	-
PAAC	-	-	0.004	-	-	-
BzP	-	1.4	-	-	-	-
Paraffin	0.25	0.25	0.25	-	-	-
Pectin degrading enzyme	0.01	0.01	0.01	0.05	0.01	0.05
Protease	0.05	0.05	0.05	-	0.1	-
Lipase	0.005	-	0.001	-	-	-
Amylase	0.003	0.001	0.01	0.02	0.01	0.015
BTA	0.15	-	0.15	-	-	-
Sulphate	23.9	23.9	23.9	31.4	17.4	-
pH (1% solution)	10.8	10.8	10.8	10.7	10.7	12.3

Example 17

The following detergent composition tablets of 25g weight were prepared in accord with the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

	I	II	III
STPP	-	48.8	47.5
Citrate	26.4	-	-
Carbonate	-	5.0	-
Silicate	26.4	14.8	25.0
Pectin degrading enzyme	0.007	0.01	0.05
Protease	0.03	0.075	0.01
Lipase	0.005	-	-
Amylase	0.01	0.005	0.001
PB1	1.6	7.8	-
PB4	6.9	-	11.4
Nonionic	1.2	2.0	1.1
TAED	4.3	2.4	0.8
HEDP	0.7	-	-
DETPMP	0.65	-	-
Paraffin	0.4	0.5	-
BTA	0.2	0.3	-
PA30	3.2	-	-
Sulphate	25.0	14.7	3.2
pH (1% solution)	10.6	10.6	11.0

Example 18

The following liquid dishwashing detergent compositions were prepared in accord with the present invention I to II, of density 1.40Kg/L :

	I	II
STPP	33.3	20.0
Carbonate	2.7	2.0
Silicate	-	4.4
NaDCC	1.1	1.15
Nonionic	2.5	1.0
Paraffin	2.2	-
Pectin degrading enzyme	0.005	0.05
Protease	0.03	0.02
Amylase	0.005	0.0025
480N	0.50	4.00
KOH	-	6.00
Sulphate	1.6	-
pH (1% solution)	9.1	10.0

Example 19

The following liquid hard surface cleaning compositions were prepared in accord with the present invention :

	I	II	III	IV	V	VI
Pectin degrading enzyme	0.005	0.01	0.02	0.02	0.005	0.005
Amylase	0.01	0.002	0.005	0.02	0.001	0.005
Protease	0.05	0.01	0.02	0.03	0.005	0.005
EDTA*	-	-	2.90	2.90	-	-
Citrate	-	-	-	-	2.90	2.90
LAS	1.95	-	1.95	-	1.95	-
C12 AS	-	2.20	-	2.20	-	2.20
NaC12(ethoxy) **sulfate	-	2.20	-	2.20	-	2.20
C12 Dimethylamine oxide	-	0.50	-	0.50	-	0.50
SCS	1.30	-	1.30	-	1.30	-
Hexyl Carbitol**	6.30	6.30	6.30	6.30	6.30	6.30
Water	Balance to 100%					

*Na4 ethylenediamine diacetic acid

**Diethylene glycol monohexyl ether

***All formulas adjusted to pH 7

Example 20

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared in accord with the present invention :

	I
Pectin degrading enzyme	0.01
Amylase	0.01
Protease	0.01
Sodium octyl sulfate	2.00
Sodium dodecyl sulfate	4.00
Sodium hydroxide	0.80
Silicate (Na)	0.04
Perfume	0.35
Water/minors	up to 100%

CLAIMS

1. A detergent composition comprising a pectin degrading enzyme having an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its optimum activity, at a pH ranging from 7 to 11.
2. A detergent composition according to claim 1 wherein said pectin degrading enzyme has an optimum activity at a pH ranging from 7 to 11.
3. A detergent composition according to claims 1-2 wherein said pectin degrading enzyme is present at a level from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of total composition.
4. A detergent composition according to any of the preceding claims further comprising a dispersant.
5. A detergent composition according to any of the preceeding claim further comprising another detergent enzyme.
6. A detergent composition according to claim 5 wherein said detergent enzyme is selected from cellulase, protease, lipase and/or amylase.
7. A detergent composition according to any of the preceding claims further comprising an enzymatic bleach system.
8. A detergent composition according to any of the preceding claims further comprising a conventional activated bleach system with a Mn-based bleach catalyst.

9. A detergent composition according to any of the preceding claims further comprising a dye transfer inhibiting polymer.

10. A detergent composition according to any of the preceding claims characterised in that said composition is in the liquid, paste, gel, bar, tablets, powder or granular form.

11. A detergent additive comprising pectin degrading enzyme having an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its optimum activity, at a pH ranging from 7 to 11.

12. Use of a detergent composition according to any of the preceding claims for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric color appearance and/or fabric dye transfer inhibition.

13. Use of a detergent composition according to claims 1-11 for cleaning hard surfaces such as floors, walls, bathroom tile and the like.

14. Use of a detergent composition according to claims 1-11 for hand and machine dishwashing.

INTERNATIONAL SEARCH REPORT

onal Application No
/US 96/12962

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C11D3/386		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 287 713 A (THE PROCTER & GAMBLE CO.) 27 September 1995 see page 3 - page 6 see page 30 - page 36 see page 47 - page 50 see claims; examples 2,3 ---	1-7,9-14
X	WO 95 09909 A (NOVO NORDISK A/S) 13 April 1995 cited in the application see page 7, line 11 - line 17 see page 19, line 10 - page 24, line 33 see claims 1,14-18 ---	1-3,5-7, 9-14
X	DE 36 35 427 A (LION CORP.) 23 April 1987 cited in the application see the whole document ---	1,5,6, 10,12
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed </div> <div style="width: 45%;"> 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. '&' document member of the same patent family </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">18 April 1997</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">14.05.97</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fac (+ 31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Serbetsoglou, A</div>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/12962

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 35362 A (GIST-BROCADES BV.) 28 December 1995 see page 6, line 19 - line 32 see page 11, line 3 - line 37 see claims 1-6,13-15 ---	1,5-7, 10,12-14
X	US 4 710 313 A (MIYAJIMA NOBUYUKI ET AL.) 1 December 1987 cited in the application see column 2, line 33 - line 44 see column 3, line 59 - line 68 ---	1,2
A	DE 39 06 124 A (WIXFORTH BRUNO) 30 August 1990 see claims 1,4 ---	1,6
A	WO 95 02044 A (NOVO NORDISK A/S) 19 January 1995 see claims 21,22,24 ---	1,5,6
A	DATABASE WPI Section Ch, Week 9142 Derwent Publications Ltd., London, GB; Class D25, AN 91-307004 XP002023059 & JP 03 205 499 A (SAWAGUCHI K.) , 6 September 1991 see abstract -----	1,5,6

INTERNATIONAL SEARCH REPORT

Annex on patent family members

Initial Application No

PCT/US 96/12962

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2287713 A	27-09-95	CA 2183747 A EP 0751990 A WO 9525790 A	28-09-95 08-01-97 28-09-95
WO 9509909 A	13-04-95	AU 7807394 A BR 9407752 A CA 2173214 A CN 1134726 A EP 0722491 A FI 961502 A	01-05-95 04-03-97 13-04-95 30-10-96 24-07-96 30-05-96
DE 3635427 A	23-04-87	JP 6039596 B JP 62091598 A	25-05-94 27-04-87
WO 9535362 A	28-12-95	AU 2886095 A CA 2193117 A EP 0766727 A FI 965042 A NO 965407 A	15-01-96 28-12-95 09-04-97 16-12-96 24-01-97
US 4710313 A	01-12-87	JP 62000913 A	06-01-87
DE 3906124 A	30-08-90	NONE	
WO 9502044 A	19-01-95	AU 7068994 A BR 9406998 A CN 1127013 A EP 0707641 A FI 960059 A JP 8512201 T NZ 267985 A	06-02-95 10-09-96 17-07-96 24-04-96 05-03-96 24-12-96 29-01-97